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Uncovering technetium binary ordered structures from first principles

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Technetium, element 43, is the only radioactive transition metal. It occurs naturally on earth in only trace amounts. Experimental investigation of its possible compounds is thus inherently difficult and limited. Half of the Tc-transition metal systems (14 out of 28) are reported to be phase-separating or lack experimental data. Using high-throughput first-principles calculations we present a comprehensive investigation of binary alloys of technetium with the transition metals. The calculations predict stable ordered structures in nine of these 14 binary systems. They also predict additional compounds in all nine known compound-forming systems and in two of the five systems reported with disordered χ or σ phases. These results accentuate the incompleteness of the current knowledge on technetium alloys. They should guide experimental studies to obtain accurate structural information on potential compounds, obviating some of the difficulties associated with such work.

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Technetium, the only radioactive transition-metal, occurs mainly in spent nuclear fuel. The practical difficulties of working with a radioactive rare material have so far hampered studies of technetium solid state physics and chemistry. In particular, exploration of technetium-based alloys has been very limited. The available experimental data indicates that 14 of the 28 Tc-transition metal binary systems are non-compound-forming^{1,2}. These systems are concentrated in columns IB, IIB, VIIB and VIIIB of the periodic table. The exceptions in these columns are Zn, reported to form two compounds with Tc, Mn which is reported with a disordered σ -phase, and Fe that forms one compound and the σ -phase. Four additional systems, Nb and the column VIB systems, are reported with a disordered σ -phase. The seven remaining binary systems of Tc with the transition metals of columns IIIB-VB are reported to be compound-forming.

Recent interest in Tc alloys has been two-fold. One motivation is a systematic basic research of fourth-row transition-metal alloys which might provide insight into the existence of general trends in material properties. Such an example is the recent surprising discovery that SrTcO₃ differs greatly from its strontium metal oxide neighbors, strontium molybdate and ruthenate. It turns out to be antiferromagnetic with the highest ordering temperature, roughly 1000K, obtained in a material without a third-row transition metal, whereas SrMoO₃ is paramagnetic with one of the highest conductivities of the metal oxides and SrRuO₃ is a metallic ferromagnet with a transition temperature around 160K³. Another motivation for Tc-alloy investigation is the search for potential candidates for long term nuclear waste dis-

posal in geological repositories by immobilization of Tc-containing residues⁴. This requires detailed knowledge of synthesis and properties of Tc alloys. Recent studies of Tc-Zr alloys⁵ and Tc deposition on gold⁶ have been carried out with this purpose in mind.

First-principles calculations based on density functional theory (DFT) provide the theoretical means to complement lacking empirical data, especially in cases where experiments are difficult. Several results on technetium and technetium alloys have been published using this approach. The zero temperature equation of state and elastic constants of pure Tc have been calculated in a study of bcc, fcc and hcp structures of 76 elements⁷, and the stability of several more complex structures has been explored in a similar work⁸. These studies verify the stability of the hcp structure for elemental Tc. A few comparative studies of technetium mono-carbides and borides, TcC, TcB₂ and TcB₄, and those of other transition metals, were aimed at revealing the origin of the well-known super-hardness of the corresponding tungsten structures⁹⁻¹¹. It was found that the Tc compounds are also potential high hardness materials. A similar study compared the properties of transition metal mononitrides¹².

In this paper we present a comprehensive investigation of binary alloys of technetium with the transition metals using high-throughput first-principles calculations. High-throughput calculations of material properties based on DFT have acquired an increasing role in recent years as an important tool for rational material development¹³⁻¹⁷. They can be used to explore the phase stability landscape of binary alloys by calculating the formation enthalpies of a large number of structures, identifying the minima

at various component concentrations. These calculations can indicate the possible existence of hitherto unidentified compounds and metastable structures and their characteristics. A previous study, using this approach, reported on twelve of the Tc-transition metal binary systems, as part of a larger review of 80 binary alloys aimed at verifying the accuracy of this method¹³. The current work covers all the Tc-transition metal alloys using PAW pseudopotentials¹⁸ and PBE-GGA exchange-correlation functionals¹⁹, vs. ultrasoft pseudopotentials and LDA exchange-correlation functionals used in¹³, and a more extensive structure database. It uncovers additional ordered structures in a few of the systems discussed in Ref.¹³ and in additional ones where experimental data is scarce and difficult to obtain.

The calculations were performed with the high-throughput framework AFLOW^{13,20} based on *ab initio* calculations of the energies by the VASP software²¹. The energies were calculated at zero temperature and pressure, with spin polarization and without zero-point motion or lattice vibrations. All crystal structures were fully relaxed (cell volume and shape and the basis atom coordinates inside the cell). Numerical convergence to about 1 meV/atom was ensured by a high energy cutoff (30% higher than the highest energy cutoff for the pseudopotentials of the components) and dense 6000 **k**-point Monkhorst-Pack meshes²².

For each system, we calculated the energies of all the reported crystal structures^{1,2} and approximately 230 additional structures from the AFLOW prototype database²⁰, listed in Ref.²³. This protocol, of searching many enumerated derivative structures and exhaustively exploring experimentally reported structures, is expected to give a reasonable balance between high-throughput speed and scientific accuracy to determine miscibility, or lack thereof, in Tc alloys (a detailed discussion on the reliability of the method appeared in Refs.^{13,24}). In Ref.¹³, it was shown that the probability of reproducing the correct ground state, if well defined and not ambiguous, is $\eta_C^* \sim 96.7\%$ [*“reliability of the method,”* Eq. (3)]. However, the existence of additional unexpected ground-states among unexplored structures can not be ruled out.

The calculations reveal stable structures both in systems known to order and those thought to be phase separating. We show that nine of the 14 technetium binary intermetallic systems reported as phase-separating in the experimental literature^{1,2} actually exhibit ordering tendencies, forming stable compounds at low-temperatures (Fig. 1). Specifically, we find additional stable structures in four systems already predicted to be ordering in¹³, Rh-Tc, Ru-Tc, Pt-Tc and Pd-Tc. The discrepancies between the current predictions and those of Ref.¹³, e.g. indication of $\text{Tc}_{24}\text{Ti}_5$ and $\text{Tc}_{24}\text{Zr}_5$ compounds, arise from the larger structure database scanned in this study. In addition, we predict unreported stable structures^{1,2} in all nine binary systems known from experiments to

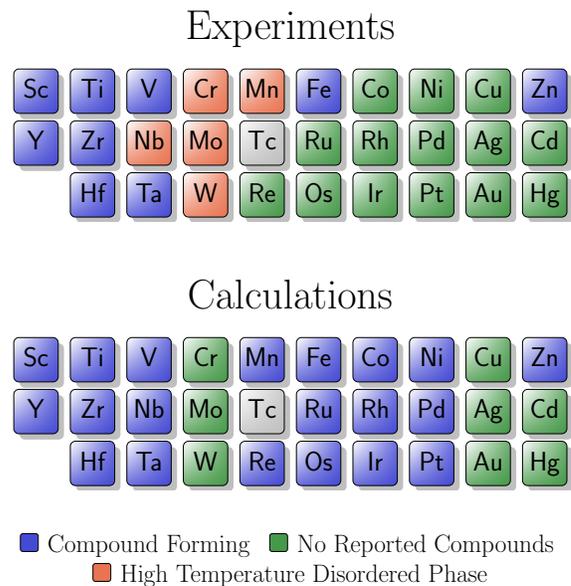


FIG. 1: (Color online) The phase-separating or compound-forming characteristics of 28 Tc - transition metal alloy systems as found in experiments and in *ab initio* calculations.

be compound-forming, and in one of the three systems exhibiting a disordered σ -phase, Mn-Tc.

The results are summarized in Table I. In the first column, the 28 alloying metals are ordered according to their Mendeleev number (or Pettifor’s chemical scale)²⁸. The next three columns indicate whether the corresponding binary system is phase separating or compound forming, according to the experimental data and to *ab initio* calculations reported here and in a previous study¹³.

The Pettifor scale is the most successful attempt to date to enable prediction of whether a newly proposed system would be compound-forming or not and the structure of the expected compounds, based on a single material parameter²⁹. Structure maps based on this scale separate well between various reported structures and thus provide a relatively high degree of predictive insight²⁸. However, the maps are purely empirical and their predictive power is limited by the availability of reliable experimental data (an assessment of the unsatisfactory current situation in this respect is given in²⁹). It is thus important to complement the sparsity of relevant experimental data with *ab initio* total energy assessments of the competing candidate structures, as we do in this paper. Ordered by this scale, Table I is divided into three parts with different experimental phase-formation characteristics. The top (systems Tc-Y to Tc-V) is occupied exclusively by compound-forming systems, except one, Nb-Tc, which is reported with a disordered χ -phase. The lower part (Os-Tc and below) is almost exclusively occupied by phase-separating systems, except one compound-forming system at the bottom, Tc-Zn. The middle part

TABLE I: Compounds observed in experiments (“Exper.”) or predicted by *ab initio* calculations (“Calc.”) in Tc binary alloys (structure prototype in parentheses. (Unkn.) denotes an unknown prototype) and their calculated tie formation enthalpies ΔH . The energy difference between a reported structure (unstable in the calculation) and a two-phase tie-line is indicated in square parentheses. A \star denotes unobserved prototypes described in^{13,23}. A \S denotes unobserved prototypes described in Table II. “-” denotes no compounds, and “N/A” no available data.

	Compounds			ΔH meV/at.
	Exper. ^{1,2}	Calc.(Previous) ¹³	Calc.(Present)	
Y	Tc ₂ Y(C14)	Tc ₂ Y(C14)	Tc ₂ Y(C14)	-176
		TcY ₃ (D0 ₁₁)	TcY ₃ (D0 ₁₁)	-86
Sc	ScTc ₂ (C14)	N/A	Sc ₃ Tc(D0 ₁₁)	-182
			Sc ₂ Tc(C11 _b)	-208
			ScTc ₂ (C14)	-304
		Sc _{0.1} Tc _{0.9} (χ)	Sc ₅ Tc ₂₄ (Re ₂₄ Ti ₅)	-189
Zr	Tc _{0.88} Zr _{0.12} (χ)		Tc ₂₄ Zr ₅ (Re ₂₄ Ti ₅)	-186
	Tc ₂ Zr(C14)	Tc ₂ Zr(C14)	Tc ₂ Zr(C14)	-314
	TcZr(Unkn.)	TcZr(B2)	TcZr(B2)	-356
		TcZr ₂ (C49)	TcZr ₂ (C49)	-271
		TcZr ₄ (D1 _a)	TcZr ₄ (D1 _a)	-186
Hf	HfTc(B2)	N/A	Hf ₃ Tc(Mo ₃ Ti [*])	-269
			Hf ₂ Tc(C49)	-357
			HfTc(B2)	-482
			HfTc ₂ (C14)	-362
		Hf _{0.1} Tc _{0.9} (χ)	Hf ₅ Tc ₂₄ (Re ₂₄ Ti ₅)	-232
Ti	Tc _{0.9} Ti _{0.1} (χ)		Tc ₂₄ Ti ₅ (Re ₂₄ Ti ₅)	-190
		Tc ₂ Ti(C11 _b)		[18]
			Tc ₅ Ti ₃ (Ga ₃ Pt ₅)	-416
	TcTi(B2)	TcTi(B2)	TcTi(B2)	-492
		TcTi ₂ (C49)	TcTi ₂ (C49)	-376
Nb	Nb _{0.15} Tc _{0.85} (χ)		Nb ₅ Tc(HfPd ₅ [*])	-144
			Nb ₃ Tc(Mo ₃ Ti [*])	-213
			Nb ₂ Tc(C11 _b)	-279
			NbTc(B2)	-365
				[19]
Ta	Ta _{0.15} Tc _{0.85} (χ)	N/A	Ta ₂ Tc(C11 _b)	-388
			TaTc(B2)	-501
V	TcV(B2)	N/A	TcV(B2)	-377
			TcV ₂ (C11 _b)	-340
			TcV ₃ (Mo ₃ Ti [*])	-266
			TcV ₄ (D1 _a)	-218
Mo	Mo _{1.5} Tc _{2.4} (A15)	N/A	-	
	Mo _{0.3} Tc _{0.7} (σ)			
W	Tc _{0.7} W _{0.3} (σ)	N/A	-	

	Compounds			ΔH meV/at.
	Exper. ^{1,2}	Calc.(Previous) ¹³	Calc.(Present)	
Cr	Cr _{0.25} Tc _{0.75} (σ)	N/A	-	
Tc	(reference)			
Re	-	N/A	ReTc ₃ (D0 ₁₁)	-5
Mn	Mn _{0.4} Tc _{0.6} (σ)	N/A	Mn ₂ Tc(C14)	-94
Fe	FeTc(B2)	N/A		[158]
	Fe _{0.4} Tc _{0.6} (σ)		FeTc ₂ (C16)	-4
Os	-	N/A	Os ₃ Tc(D0 ₁₉)	-71
			OsTc(B19)	-83
			OsTc ₃ (D0 ₁₉)	-57
Ru	-	Ru ₃ Tc(D0 ₁₉)	Ru ₃ Tc(D0 ₁₉)	-63
			RuTc(B19)	-73
			RuTc ₃ (D0 ₁₉)	-47
			RuTc ₅ (RuTc ₅ [§])	-32
Co	-	N/A	CoTc(B19)	-46
			CoTc ₃ (D0 ₁₉)	-53
Ir	-	N/A	Ir ₈ Tc(Pt ₈ Ti)	-89
			Ir ₂ Tc(Ir ₂ Tc [§])	-224
			IrTc(B19)	-287
			IrTc ₃ (D0 ₁₉)	-217
Rh	-	Rh ₂ Tc(ZrSi ₂)	Rh ₂ Tc(Ir ₂ Tc [§])	-157
			RhTc(B19)	-175
			RhTc ₃ (D0 ₁₉)	-158
Ni	-	N/A	Ni ₄ Tc(D1 _a)	-30
			NiTc ₃ (D0 ₁₉)	-106
Pt	-	Pt ₃ Tc(FCC _{AB3} ^[001])	Pt ₃ Tc(BCC _{AB3} ^[001])	-158
			Pt ₂ Tc(CuZr ₂)	-184
			PtTc ₃ (D0 ₁₉)	-267
Pd	-	PdTc ₃ (D0 ₁₉)	PdTc(RhRu [*])	-63
			PdTc ₃ (D0 ₁₉)	-73
Au	-	-	-	
Ag	-	-	-	
Cu	-	-	-	
Hg	-	-	-	
Cd	-	-	-	
Zn	-	N/A	Tc ₂ Zn(FCC _{AB2} ^[100])	-42
			TcZn ₃ (L1 ₂)	-62
			TcZn ₇ (CuPt ₇)	-55
			TcZn ₇ (CuPt ₇)	-55
			TcZn ₁₅ (Unkn.)	

is a border zone of six systems (Mo-Tc to Fe-Tc), four of which exhibit a disordered σ -phase, one, Fe-Tc, reported with a single compound in addition to the σ -phase, and one, Re-Tc, phase-separating.

The picture emerging from the calculations is considerably different. Ordered structures are predicted in the three lower systems of the of the middle part, Re-Tc, Mn-Tc and Fe-Tc, and in the eight upper systems of the lower part, Os-Tc to Pd-Tc, thus predicting a cluster of eleven compound-forming systems in the middle

of the table. Stable structures MTc_3 of prototype D0₁₉ are found for eight of the nine column VIII transition metals, except Fe. For two of them, Os and Ru, the structure M_3Tc with the same prototype is also stable. Three of the compounds in this cluster, RuTc₅, Ir₂Tc and Rh₂Tc, are predicted with crystal structures that have no known prototype or *Strukturbericht* designation. They were found among the symmetrically distinct fcc-, bcc- and hcp-based superstructures included in the AFLOW database¹³. These structures are described in Table II.

TABLE II: Geometry of new prototypes marked by § in Table I. Atomic positions and unit-cell parameters are fully relaxed.

Formula	RuTc ₅	Ir ₂ Tc
Lattice	Monoclinic	Orthorhombic
Space Group (opt.)	Cm No.8 (2)	Cmcm No.63
Pearson symbol	mS12	oS12
HT lattice type/variation ²⁵	MCLC/MCLC1	ORCC/ORCC
Conv. Cell <i>a, b, c</i> (Å) <i>α, β, γ</i> (deg)	9.997, 2.752, 6.484 90 75.942 90	2.751,14.374,4.381 90, 90, 90
Wyckoff positions ^{26,27}	Ru1 0,0,-0.00140 (2a) Tc1 0.390,0 -0.277 (2a) Tc2 -0.335,0,-0.331 (2a) Tc3 0.055,0,0.388 (2a) Tc4 0.334,0,0.334 (2a) Tc5 -0.278,0,0.055 (2a)	Ir1 0,0.998,1/4 (4c) Ir2 0,0.668,1/4 (4c) Tc1 0,0.334,1/4 (4c)
AFLOW label ²⁰	"128"	"143"

We also find stable ordered structures in Nb-Tc, indicating a continuous cluster of eight compound-forming systems at the top. Within this cluster, the metals of the VB column order into structure $M_2\text{Tc}$ of prototype C11_b, and those of the IIIB and IVB columns, except Ti, form a stable structure $M\text{Tc}_2$ of prototype C14. Six of these eight systems are reported with the disordered χ -phase (*Strukturbericht* A12, space group I43m). In four of them we find stable structures of prototype Re₂₄Ti₅, which is an ordered realization of this phase. This indicates that the χ -phase regime of stability extends to the low-temperature region of these binary phase-diagrams. In the other two systems, Nb-Tc and Ta-Tc, this structure has a higher formation enthalpy than the two-phase region tie-line, indicating decomposition of the χ -phase at low-temperatures. Experimental studies of the Tc-Zr system report a structure, denoted Tc₆Zr, with the crystallographic characteristics of the χ -phase and a wide range of stoichiometries⁵. Our calculations thus identify

the prototype and confirm the existence of a corresponding ordered structure at low temperatures. Similar behavior should be expected in the adjacent systems, Sc-Tc, Hf-Tc and Tc-Ti.

The remaining phase-separating systems form two small groups. One in the middle of the table, of three systems reported with a σ -phase and predicted to have no ordered stable structures. The other, near the bottom, includes five systems for which both experiments and calculations indicate no compound formation. The Tc-Zn system remains an isolated compound-forming system at the last row of Table I. For this system, the calculations predict two ordered structures, Tc₂Zn and TcZn₃ in addition to the observed one TcZn₇. We find no stable structures in the vicinity of TcZn₁₅, reported in experiments with an unidentified prototype.

The almost perfect grouping of systems into four well-defined clusters by their predicted phase-formation characteristics nicely complements the trends indicated by the Pettifor chemical scale. It reverses the ratio of phase-separating to compound-forming systems from the experimental database.

Empirical data on technetium alloy properties is incomplete and difficult to obtain due the radioactivity of the element. Generating such data using *ab initio* electronic structure calculations is thus of special interest. In this paper, we present results of a computational high-throughput study on phase ordering in Tc alloys that are considerably different from those reported in current experimental data. These theoretical predictions should serve as guide for future studies of these materials and as the starting point for designing desirable alloys for various potential applications.

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